Study of Tetragonally Compressed Complexes of Fe(II), Ni(II) and Cu(II)

SUDAMA CAUDHRY1, SUMIT KUMAR SINHA1, PARVEEN KUMAR1, PUNIT KUMAR1, TRILOK PRASAD2 and SHIVADHAR SHARMA1,*

1Department of Chemistry, Magadh University, Bodh Gaya-824 234, India
2Department of Chemistry, Ram Nagina Singh College, Maner, Patna-801 111, India

*Corresponding author: Tel: +91 631 2220039; E-mail: sharma.shivadhar@gmail.com

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INTRODUCTION

The degeneracy of orbitals can be removed by the lowering of symmetry of molecules. This can be achieved by Jahn-Teller distortion theorem. This may be stated as – “In a non-linear molecule if degenerate orbitals are asymmetrically occupied a distortion occurs to remove the degeneracy.” or it may also be stated as “In an electronically degenerated state a non-linear molecule undergoes distortion to remove the degeneracy by lowering the symmetry and thus by lowering the energy” [1-3]. The distortion may also be caused by putting different ligands in XY-plane and along Z-axis as they are likely to produce crystal field of different strength in XY-plane and along Z-axis. The tetragonally distortion may either be Z-out distortion or Z-in distortion depending upon elongation along Z-axis or compression along Z-axis. The elongation along Z-axis is most preferred and has been widely studied in respect of Z-in distortion [4-8].

Semicarbazones and thiosemicarbazones have emerged as promising ligands in the coordination chemistry in the light of their excellent binding capability. The literature survey revealed a plethora of work in the field of semicarbazones and thiosemicarbazones and their transition metal complexes because of their fascinating structural properties and broad spectrum of their application in various field [9-15]. Due to their pharmaceutical properties which are frequently higher for the metal complexes than the free ligands, they have extensively been studied during recent years.

The present paper deals with the synthesis, structural and biological evaluation of tetragonally compressed octahedral complexes of 4’-nitrobenzaldehyde-4-phenylsemicarbazone and 4’-nitrobenzaldehyde-4-phenylthiosemicarbazone with Fe(II), Ni(II) and Cu(II).

EXPERIMENTAL

All the chemicals used were of AnalyR Grade. 4’-Nitrobenzaldehyde was procured from Fluka and 4-phenylsemicarbazide and 4-phenylthiosemicarbazide were purchased from Aldrich. Fe(CH₃COO)₂, Ni(CH₃COO)₂ and Cu(CH₃COO)₂ were purchased from E. Merck. All the chemicals were used without further purification. The ligand 4’-nitrobenzaldehyde-4-phenylthiosemicarbazone was prepared by refluxing the mixture of equimolar solution of nitrobenzaldehyde and 4-phenylthiosemicarbazide in ethanol in the presence of few drops of cone. H₂SO₄ for 1 h (Scheme-1). The solid obtained on cooling the solution was recrystallized in ethanol into yellowish white crystal with 85 % yield.

The other ligand i.e., 4’-nitrobenzaldehyde-4-phenylthiosemicarbazone was prepared by the similar method of reflux like above wherein 4-phenylsemicarbazide was replaced by 4-phenylthiosemicarbazide. The crude solid was recrystallized...
in ethanol whereby light yellow crystal were obtained with 86% yield.

Both ligands were used for complexation with Fe(II), Ni(II) and Cu(II) by the usual method of refluxing, the mixture of metal(II) acetate with ligands taken in 1:2 ratio in ethanol for 3-4 h. The precipitate was dried in desiccators on anhydrous calcium chloride. The yields were 74-80%. Their melting point was recorded.

**Physical and analytical measurements:** C, H, N content of ligands and complexes was determined using Perkin-Elementer 2400 CHN Elemental Analyzer. Iron was estimated by volumetrically using N/10 K₂Cr₂O₇ solution. Copper was estimated iodometrically using standard thiosulphate solution. Cobalt was estimated gravimetrically using α-nitroso β-naphthol. The molar conductivity of complexes was determined using Perkin-Elementer FTIR-Spectrometer, Spectrum-two in range of 4000-400 cm⁻¹ using KBr Pellets. The electronic spectra of complexes were recorded on Perkin-Elmer UV visible Spectrometer Lambda-25 using DMSO solution. The magnetic susceptibility of complexes was determined on Gouy balance at room temperature using mercury tetra-thiocynatocobaltate as calibrate.

**RESULTS AND DISCUSSION**

The percentage composition of ligands and complexes have been displayed in Table-1. On the basis of percentage composition and molar conductivities values, the complexes have been formulated as [ML₂X₂] where M = Fe(II), Ni(II) and Cu(II), L = NBPS or NBPTS and X = CH₃COO⁻. The conductivity values of complexes are too low which indicate their non-electrolytic nature [16-19].

**IR spectra of ligands and complexes:** The IR spectra of free ligand 4’-nitrobenzaldehyde-4-phenyl semicarbazone a sharp band appears at 3150 cm⁻¹ which is assigned to ν(N-H) [20]. It is further supported by a medium band at 1555 cm⁻¹ due to bending vibration of δ(N-H). The strong band appearing at 3035 cm⁻¹ is due to ν(C-H) stretching of benzene ring [21,22]. The medium band appearing at 2845 cm⁻¹ is due to ν(C-H) of azomethine group. The strong band appearing at 1665 cm⁻¹ is fairly assigned to ν(C=O) stretching of semicarbazone [23]. In the IR spectra of complexes of NBPS this band undergoes negative shift and appears at 1640 cm⁻¹ which is indicative of its coordination to the metal ions through oxygen [24,25]. The medium band appearing at 1630 cm⁻¹ in the IR spectra of free ligand is attributed to ν(C=N) of azomethine group of the ligand [26]. In the IR spectra of complexes this band shifts to a lower frequency and appears at 1600 cm⁻¹. This shows the coordination of the ligand through azomethine nitrogen [27,28]. The medium and weak bands appearing at 1580, 1510 and 1455 cm⁻¹ are the characteristic absorption frequency of benzene ring vibration. The sharp band appearing at 1535 and 1340 cm⁻¹ may be assigned to ν(CO)(NO₂) and ν(NH)(NO₂) respectively. In the IR spectra of 4’-nitrobenzaldehyde-4-phenyl thiosemicarbazone the band near 1665 cm⁻¹ doesn’t appear which shows the absence of C=O group in this ligand. This ligand absorbs strongly at 1230 cm⁻¹ due to ν(C=S) stretching, which undergoes negative shift in its complexes. It is indicative of coordination through sulphur of C=S group of this ligand to the metal ions [29]. In the spectra of all the complexes two new bands appear at 1335 and 1330 cm⁻¹. These bands are the characteristic absorption bands for monodentately coordinated CH₃COO⁻ ion to the metal ion in all the complexes. Thus on the basis of IR spectra of complexes in comparison to that of the free ligands, it may be asserted that the ligand NBPS acts as bidentate neutral ligand co-ordinating through carbonyl oxygen and azomethine nitrogen while the second ligand NBPTS also

![Scheme-I: Structure of 4’-nitrobenzaldehyde-4-phenyl semicarbazone (NBPS) and 4’-nitrobenzaldehyde-4-phenyl thiosemicarbazone (NBPTS)](image)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>M (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>λₚ (Ω⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBPS</td>
<td>Yellowish white</td>
<td>85</td>
<td>176</td>
<td>–</td>
<td>89.82</td>
<td>3.98</td>
<td>19.42</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NBPTS</td>
<td>Light yellow</td>
<td>86</td>
<td>198</td>
<td>3.89</td>
<td>18.46</td>
<td>10.59</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Fe(NBPS)₂(CH₃COO)₃]</td>
<td>Brilliant green</td>
<td>74</td>
<td>240</td>
<td>5.19</td>
<td>14.97</td>
<td>–</td>
<td>15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Fe(NBPTS)₂(CH₃COO)₃]</td>
<td>Dull green</td>
<td>80</td>
<td>242</td>
<td>4.91</td>
<td>14.29</td>
<td>8.12</td>
<td>16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Ni(NBPS)₂(CH₃COO)₃]</td>
<td>Dull red</td>
<td>80</td>
<td>240</td>
<td>5.17</td>
<td>14.87</td>
<td>–</td>
<td>13</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Ni(NBPTS)₂(CH₃COO)₃]</td>
<td>Light red</td>
<td>78</td>
<td>246</td>
<td>4.98</td>
<td>14.28</td>
<td>8.12</td>
<td>15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Cu(NBPS)₂(CH₃COO)₃]</td>
<td>Bright blue</td>
<td>74</td>
<td>248</td>
<td>4.86</td>
<td>14.79</td>
<td>–</td>
<td>15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Cu(NBPTS)₂(CH₃COO)₃]</td>
<td>Blue</td>
<td>76</td>
<td>252</td>
<td>4.91</td>
<td>14.12</td>
<td>8.00</td>
<td>17</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
acts as bidentate neutral ligand coordinating through thiosulphur and azomethine nitrogen forming 5-membered chelate ring.

**Magnetic moment and electronic spectra:** The magnetic moment and electronic spectra of Fe(II) complexes have been given in Table-2.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(v_1) (cm(^{-1}))</th>
<th>(v_2) (cm(^{-1}))</th>
<th>(v_3) (cm(^{-1}))</th>
<th>(\mu) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(NBPS)(_2)(CH,COO)(_2)</td>
<td>5600</td>
<td>9800</td>
<td>12800</td>
<td>5.08</td>
</tr>
<tr>
<td>Fe(NBPTS)(_2)(CH,COO)(_2)</td>
<td>5400</td>
<td>9200</td>
<td>12600</td>
<td>5.07</td>
</tr>
</tbody>
</table>

The magnetic moment of Fe(II) complexes are found to be 5.07 and 5.08 BM which correspond to high spin octahedral geometry to these complexes [30,31]. Fe(II) is a \(d^6\) system for which the ground state term is \(^5D\) which splits into \(^5T_{2g}\) and \(^5E\) and thus only one band is expected in Fe(II) complexes. But here the complexes display three bands which indicates that the complexes have undergone tetragonal distortion (\(D_{5d}\)). This causes further splitting of \(^5T_{2g}\) in \(^5B_2g\) and \(^5E\) while, the excited state \(^5E\) splits into \(^5B_1g\) and \(^5A_1g\). Thus these three bands may be assigned to \(^5B_1g\) = \(v_1\), \(^5B_2g\) = \(v_2\) and \(^5A_1g\) = \(v_3\) [32]. \(v_1\) is the major of 10 \(Dq\), while \(v_1\) and \(v_2\) involve also the other parameters like \(D_1\) and \(D_2\). The values of different crystal field parameters are given in Table-3.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(Dq_1) (cm(^{-1}))</th>
<th>(Dq_2) (cm(^{-1}))</th>
<th>(D_{1}) (cm(^{-1}))</th>
<th>(D_{2}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(NBPS)(_2)(CH,COO)(_2)</td>
<td>980</td>
<td>1650</td>
<td>1229</td>
<td>-383</td>
</tr>
<tr>
<td>Fe(NBPTS)(_2)(CH,COO)(_2)</td>
<td>920</td>
<td>1490</td>
<td>1257</td>
<td>-326</td>
</tr>
</tbody>
</table>

In these complexes the greater value of \(Dq_2\) than \(Dq_1\) and negative value of \(D_1\) conspicuously indicate tetragonal compression along Z-axis in octahedral symmetry.

The magnetic moment and electronic spectra of Ni(II) complexes have been displayed in Table-4.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(v_1) (cm(^{-1}))</th>
<th>(v_2) (cm(^{-1}))</th>
<th>(v_3) (cm(^{-1}))</th>
<th>(\mu) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NBPS)(_2)(CH,COO)(_2)</td>
<td>11550</td>
<td>14550</td>
<td>16600</td>
<td>24170</td>
</tr>
<tr>
<td>Ni(NBPTS)(_2)(CH,COO)(_2)</td>
<td>11300</td>
<td>14560</td>
<td>16300</td>
<td>24100</td>
</tr>
</tbody>
</table>

The magnetic moment and electronic spectral bands of Cu(II) complexes have been displayed in Table-6.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(v_1) (cm(^{-1}))</th>
<th>(v_2) (cm(^{-1}))</th>
<th>(v_3) (cm(^{-1}))</th>
<th>(\mu) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NBPS)(_2)(CH,COO)(_2)</td>
<td>7200</td>
<td>18600</td>
<td>21000</td>
<td>1.96</td>
</tr>
<tr>
<td>Cu(NBPTS)(_2)(CH,COO)(_2)</td>
<td>7000</td>
<td>18250</td>
<td>21100</td>
<td>1.98</td>
</tr>
</tbody>
</table>

The appearance of three bands is clearly the consequence of tetragonal distortion in \(O_h\) symmetry while the greater value of \(Dq\), than \(Dq_0\) with negative value of \(D_1\) show without doubt that there is compression along Z-axis of \(O_h\) symmetry [40,41].

**Biological evaluation:** The ligands as well as their metal complexes were screened against Gram-positive bacteria Staphylococcus aureus and Gram-negative bacteria Escherichia coli at concentration 50 and 100 ppm in DMSO and the results were compared with streptomycin as standard. The activity index of ligands as well as their metal complexes was derived by the expression:

\[
\text{Activity index} = \frac{\text{Inhibition zone by test compound (diameter)}}{\text{Inhibition zone by control (diameter)}} \times 100
\]

The results displayed in Table-8 clearly indicates that both ligands are biological active. It also indicates that the antibacterial activity gets enhanced after complexation. The activity increases with increasing concentration of ligands and complexes, however all the ligands and complexes show less antibacterial activity in comparison to the standard. The thio ligand and its metal complexes record greater activity than semicarbazone ligand and their complexes, which may be due to the presence of sulphur in place of oxygen in thiosemicarbazone. Copper complex with thiosemicarbazone shows

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(v_1) (cm(^{-1}))</th>
<th>(v_2) (cm(^{-1}))</th>
<th>(v_3) (cm(^{-1}))</th>
<th>(\mu) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NBPS)(_2)(CH,COO)(_2)</td>
<td>11550</td>
<td>14550</td>
<td>16600</td>
<td>24170</td>
</tr>
<tr>
<td>Ni(NBPTS)(_2)(CH,COO)(_2)</td>
<td>11300</td>
<td>14560</td>
<td>16300</td>
<td>24100</td>
</tr>
</tbody>
</table>
the greatest activity than all other complexes which may be due to a toxic nature of copper metal. The increases in antibacterial activity of ligands after complexation may be attributed to the formation of chelates in complexes [12,22].

Conclusion

The study reveals that the ligands are weakly coordinated to the metal ions in XY plane than acetate ions along Z-axis due to the presence of strongly electron withdrawing-N O group in planar ligands. This makes tetragonally distorted octahedral complexes with appreciable compression along Z-axis which is well supported by the higher values of Dq (xy) than Dq(z) and negative value of Δ in all the complexes. The antibacterial screening of complexes reveals that all the complexes have greater antibacterial activity than the free ligands confirming the concept of enhancement of antibacterial activities of a compound after complexation.

REFERENCES